RE-INVESTIGATING THE PROCESS IMPACTS FROM OXALIC ACID HIGH LEVEL WASTE TANK CLEANING

E Ketusky*
Washington Savannah River Company

Keywords
Oxalate
Oxalic Acid
Precipitate
Vitrification
H2
CO2

Correspondence to:*
E Ketusky
Washington Savannah River Company
766-H Aiken, SC, 29806
email: edward.ketusky@srs.gov

ABSTRACT

The impacts and acceptability of using oxalic acid to clean the Savannah River Site, High Level Waste Tanks 1-8, were re-investigated using a two-phased approach. For the first phase, using a representative Tank 1-8 sludge, the chemical equilibrium based software, OLI ESP© and Savannah River Site laboratory test results were used to develop a chemically speciated material balance and a general oxalate mass balance. Using 8 wt% oxalic acid with a 100% molar excess, for every 1 kg of sludge solid that was dissolved, about 3.4 kg of resultant solids would form for eventual vitrification, while about 0.6 kg of soluble oxalate would precipitate in the evaporator system, and form a salt heel. Using available analyses, a list of potential safety and process impacts were developed, screened, and evaluated for acceptability.

The results showed that the use of oxalic acid had two distinct types of impacts, those which were safety based and required potential upgrades or additional studies. Assuming such were performed and adequate, no further actions were required. The second type of impacts were also acceptable, but were long-term, and as such, would need to be managed. These impacts were directly caused by the solubility characteristics of oxalate in a concentrated sodium solution and, occurred after pH restoration. Since oxalate destruction methods are commonly available, their use should be considered. Using an oxalate destruction method could enable the benefits of oxalic to applied, while eliminating the long-term impacts that must be managed, and hence should be considered.

INTRODUCTION

The Savannah River Site has approximately 49 High Level Waste tanks currently not decommissioned. Half of these tanks were built in the 1950's, while the others were built in the 1970's. The tanks are 23- to 26-meters in diameter and 7- to 10-meters tall. Each has a 2.8E+6 - to 4.9E+6 -liter capacity, is made of carbon steel, and typically contains miles of carbon steel cooling coils. All are located subsurface. Sixteen of the tanks have developed leak sites, adding to the urgency of emptying the tanks (Ref. 1).

SRS HLW tanks must be very clean in order to support closure, due to the high specific activity of the residual waste and the close proximity to the water table. For closure, the residual volume in most tanks must be 190 to 1,900 liters (or less), which translates to 0.02 to 0.2 cm of waste, if the waste were spread evenly on the tank bottom. To aid in the removal, the use of oxalic acid is being considered a solvent. Oxalic acid is preferred because of its combined cleaning and chelating effects **(**Ref. 2**)**, as well as its ability to form a passivation layer on carbon steel (Ref. 3). Additionally, less than 30 years ago, its use was proven very successful in cleaning an SRS HLW tank **(**Ref. 1).

When oxalic acid proved successful in the 1970s, it was deemed so based almost entirely on the cleaning effectiveness, as the downstream disposal process for sludge solids was not developed (Ref. 4). Its success did not include the evaluation of the current well-defined disposal path. Since 1988, the disposal process for HLW sludge solids (*i.e.*, glass vitrification at the Defense Waste Processing Facility (DWPF)) has become operational. Additionally, since the 1970's, the allowed operating parameters and safety controls have become much more formalized. Currently, because of these changes to the process, there is much debate as to the acceptability of using oxalic acid on the HLW process. A new research effort, therefore, was initiated to re-investigate the impacts and acceptability of using oxalic acid. Since Tanks 1-8 would be the first to be cleaned, they were evaluated.

APPROACH

The approach used to re-investigate the impacts was two-fold. It consisted of the following:

Construct a detailed material balance, analyzing chemical species of interest and the mass of resultant solids, while encompassing all of the impacted processes.

Identify the potential impacts, screening them for likelihood, and evaluating them for acceptability.

In constructing the material balance, a block flow diagram was developed. The scope included the initial treatment activities, the pH restoration activities, and the impacted downstream activities. Process records and available sludge sample results (Ref. 5) were used to identify a representative chemical characterization of the sludge. Using Version 6.7 of OLI Environmental Simulation Process (ESP)®, a commercially available chemical equilibrium-based software, and Savannah River National Laboratory (SRNL) dissolution test results to validate the amount of acid required (Ref. 2 & 3), a chemically speciated material balance for the *Treatment Tank* and *pH Restoration Tank* was developed. The results showed that two ultimate waste streams developed.

The two waste streams formed, largely equated to the solubility of oxalates in high sodium concentration solutions (*i.e.,* one with a high concentration of precipitated oxalates, and one with a low concentration of soluble oxalates). Solids, transferred as a sludge slurry, would become part of a feed batch for vitrification at the *Defense Waste Process Facility (DWPF)*, while the aqueous solutions would be added to the *Evaporator Drop Tank*, where even more oxalate precipitates would form.

A list of potential system and process impacts were developed (Ref. 6). The impacts were first screened based using references which discounted the issue or the potential. Taking advantage of the material balance and oxalate balance, impacts that could not be screened-out, received a detailed evaluation for acceptability. Since all of the impacts were deemed acceptable, the use of

oxalic acid was also deemed acceptable. After the acceptability of using oxalic acid was determined, a general recommendation, based on the overall observations associated with the acceptability, was made.

MATERIAL BALANCE

Characterization of the Sludge

Process records and sample results were used to determine a hypothetical representative sludge for Tanks 1-8 (Ref. 5&6). The goal in developing a composition for hypothetical representative waste was to account for at least 85 wt% of the solids mass, as well as ensure any constituents that were believed to significantly impact behavior, were also considered. Because of the sludge aging/morphology process, a density (*i.e.*, mass of "dry sludge" per "gallon of sludge waste") consistent with the process database for averaged assumed density for aged waste was applied (*i.e.,* 60% of the mass for slurry is assumed to be from water). In general, the Tanks 1-8 sludge consists of the general metal discards with a large depleted uranium concentration. Table 1 provides a characterization used for the representative sludge.

Table 1 Representative Sludge Constituents

Constituent	Solids (wt%)	Total (wt%)
H2O	NA	60
Al(OH)3	13.3	5.3
CaCO3	5.3	2.1
Ce(OH)3	0.4	0.1
Fe(OH)3	51.3	20.5
Hg0	0.1	0
MnO2	6.2	2.5
NaCl	1.8	0.7
NaNO3	1.6	0.7
NaOH	5.1	2.0
Ni(OH)2	4.2	1.7
SiO2	1.8	0.7
UO2(OH)2	9.0	3.6
Total	100%	100%
Total kg	9.4E+3	1.8E+4

As shown in Table 1, the representative sludge contains very high concentrations of iron (up to 52 wt% of the solids), high concentrations of depleted uranium (up to 12 wt% of the solids), but relatively low concentrations of aluminum (less than 14 wt% of the solids).

Flow Diagram

Since, the pH of the dissolved heel would be restored using a 50 wt% caustic solution and only available existing transfer lines would be used, there are only be two possible paths for the oxalates out of the HLW process, both are shown in Figure 1.

The impacts and acceptability of using oxalic acid to clean the Savannah River Site, High Level Waste Tanks 1-8, were re-investigated using a two-phased approach. For the first phase, using a representative Tank 1-8 sludge, the chemical equilibrium based software, OLI ESP© and Savannah River Site laboratory test results were used to develop a chemically speciated material balance and a general oxalate mass balance. Using 8 wt% oxalic acid with a 100% molar excess, for every 1 kg of sludge solid that was dissolved, about 3.4 kg of resultant solids would form for eventual vitrification, while about 0.6 kg of soluble oxalate would precipitate in the evaporator system, and form a salt heel. Using available analyses, a list of potential safety and process impacts were developed, screened, and evaluated for acceptability.

The results showed that the use of oxalic acid had two distinct types of impacts, those which were safety based and required potential upgrades or additional studies. Assuming such were performed and adequate, no further actions were required. The second type of impacts were also acceptable, but were long-term, and as such, would need to be managed. These impacts were directly caused by the solubility characteristics of oxalate in a concentrated sodium solution and, occurred after pH restoration. Since oxalate destruction methods are commonly available, their use should be considered. Using an oxalate destruction method could enable the benefits of oxalic to applied, while eliminating the long-term impacts that must be managed, and hence should be considered.

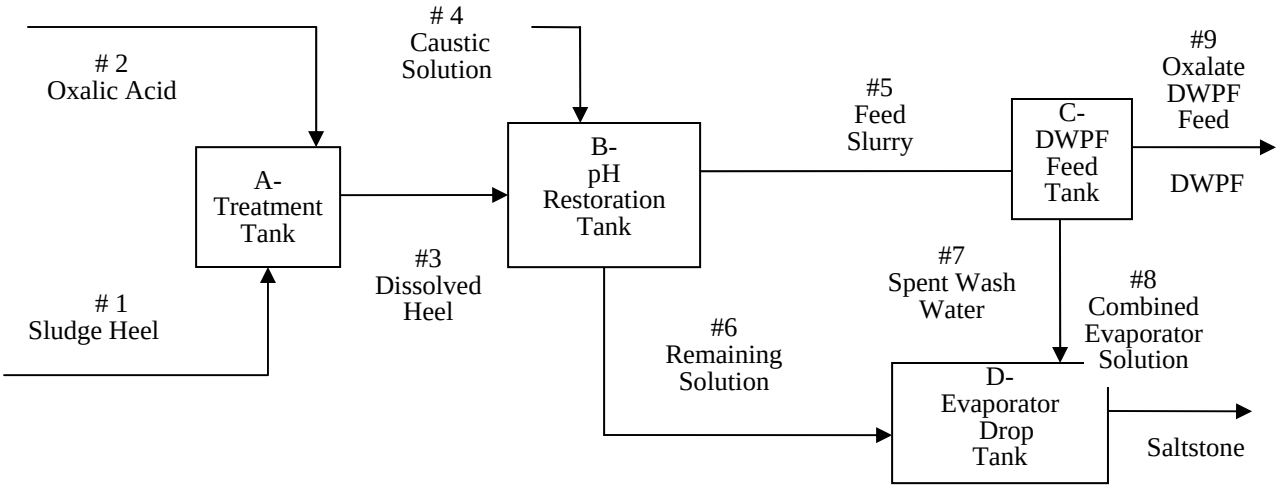

Figure 1. Oxalic Acid Cleaning Flow Diagram

As shown in Figure 1, the *#2 Oxalic Acid* is added to the *#1 Sludge Heel* in the *A-Treatment Tank*. After the sludge heel dissolves, the *#3 Dissolved Heel* is transferred to the *B-pH Restoration Tank*, which has been pre-treated with the *#4 Caustic Solution.* Within the *B-pH Restoration Tank* much of the oxalate precipitates as sodium oxalate. Within the *B-pH the Restoration Tank, the* precipitate slurry, the *#5 Feed Slurry*, is made and transferred to the *C-DWPF Feed Tank*, while the liquid remaining, the *#6 Remaining Solution*, is transferred to the *D-Evaporator Drop Tank*. The *#7 Spent Wash Water* is decanted from the *C-DWPF Feed Batch* to the *D-Evaporator Drop Tank* resulting in the *#8 Combined Evaporator Solution.* The oxalate solids are fed to DWPF as #9 *Oxalate DWPF Feed.*

Assumptions used to model the process and prepare the material balance include:

- The solvent, the *#2 Oxalic Acid* addition of 8wt% acid, is sized for 100% molar excess.
- Adequate time is allowed for the dissolution reaction in *A-Treatment Tank* to reach equilibrium.
- The *#4 Caustic Solution* (50 wt%) is pre-added to an empty *B-pH Restoration Tank* and given adequate time to react with the *#3 Dissolved Heel*, reaching equilibrium and resulting in 0.1 M free hydroxide, as required by the corrosion control program (Ref. 7).

- The *#5 Feed Slurry* is 16 wt% solids slurry and is used to transfer the solid oxalates to *C-DWPF Feed Tank* already containing a pre-washed and pre-qualified sludge batch.
- All solution used as part of the 16wt% solids slurry *in #5 Feed Slurry* to the *C-DWPF Feed Tank* is decanted as *#7 Spent Wash Water*, such that *#9 Oxalate DWPF Feed* contains only solid oxalates.

Using the representative sludge in Table 1, the Figure 1 flow diagram, the chemical equilibrium software, with the model input and assumptions, a speciated material balance was determined for *Streams #1 through #6.* This is shown as Table 2.

Table 2 Speciated Material Balance for Streams #1-6

Stream	*# 1 Sludge Heel*		*# 2 Oxalic Acid*	*#3 Dissolved Heel*		*# 4 Caustic Solution*	*#5 Feed Slurry*		*#6 Remaining Solution*
Phase	*Aqueous*	*Solid*	*Aqueous*	*Aqueous*	*Solid*	*Aqueous*	*Aqueous*	*Solid*	*Aqueous*
Unit	Weight Fraction								
H2O	9.3E-1	6.2E-2	9.2E-1	9.1E-1	0	0	9.6E-1	9.6E-1	9.6E-1
H2C2O4	0	0	0	8.0E-2	4.0E-2	0	0	0	0
HCl	0	0	0	4.6E-4	0	0	0	0	0
HNO3	0	0	0	4.8E-4	0	0	0	0	0
Na2CO3	3.4E-4	0	8.0E-2	0	0	0	2.1E-3	0	2.1E-3
NaCl	1.2E-2	0	0	0	0	0	7.1E-4	0	7.1E-4
NaNO2	0	0	0	0	0	0	0	0	0
NaNO3	1.1E-2	0	0	0	0	0	6.2E-4	0	6.2E-4
NaOH	3.4E-2	0	0	0	0	5.0E-1	4.6E-3	0	4.6E-3
Na2C2O4	0	0	0	4.4E-3	0	0	2.9E-2	7.0E-1	2.9E-2
Al(OH)3	0	1.5E-1	0	0	0	0	4.2E-2	0	0
AlOOH	0	0	0	4.1E-3	0	0	0	0	0
NaAlO2	3.3E-3	0	0	0	0	0	6.6E-4	0	6.6E-4
CaC2O4	0	0	0	4.1E-4	0	0	7.6E-7	2.4E-2	7.6E-7
CaCO3	0	6.2E-2	0	0	2.8E-1	0	0	0	0
Ca(OH)2	2.4E-4	0	0	0	0	0	0	0	0
Ce2O3	1.3E-3	0	0	0	0	0	7.6E-5	0	7.6E-5
Ce2(C2O4)	0	0	0	3.8E-5	9.1E-3	0	0	0	0
Fe2(C2O4)	0	0	0	3.8E-2	0	0	2.6E-5	0	2.6E-5
Fe(OH)3	7.4E-5	5.8E-1	0	0	0	0	0	1.7E-1	0
MnC2O4	0	0	0	4.5E-4	3.4E-1	0	2.8E-6	0	2.8E-6
Mn(OH)2	8.8E-7	6.0E-2	0	0	0	0	0	1.8E-2	0
NiC2O4	0	0	0	5.7E-5	2.9E-1	0	9.5E-8	0	9.5E-8
NiOH2	3.1E-7	4.5E-2	0	0	0	0	0	1.4E-2	0
SiO2	1.2E-2	0	0	3.8E-3	8.0E-2	0	7.1E-4	0	7.1E-4
UO2C2O4	0	0	0	3.8E-3	0	0	1.1E-4	0	1.1E-4
UO2OH2	2.7E-8	9.9E-2	0	0	0	0	0	2.9E-2	0
Total kg	1.7E+4	9.4E+3	2.6E+5	2.9E+5	2.6E+3	3.9E+4	1.6E+5	3.2E+4	1.4E+5
Oxalate kg	0	0	2.1E+4	1.9E+4	1.5E+3	0	3.0E+3	1.5E+4	2.7E+3

As shown in Table 2, at 100% excess acid, some oxalate will precipitate in the *A-Treatment Tank* (*i.e., #3 Dissolved Heel-Solid*). This phenomena was also observed in laboratory dissolution tests as a white suspension, but was confirmed to be easily transferred (Ref. 8). By comparing the total kg in *#1 Sludge Heel-Solid* in Table 2 to the total kg *#5 Feed Slurry-Solid*, we see that for 1 kg of solid sludge dissolved, 3.4 kg of solids would be fed to DWPF.

Since the evaporator system is constantly receiving new feed, its aqueous sodium concentration greatly varies. Oxalate solubility is largely a function of the sodium concentration (Ref. 9), as shown in Figure 2 (Ref. 6). To understand the general impact of oxalic acid on the evaporator system, a solubility based oxalate balance was developed.

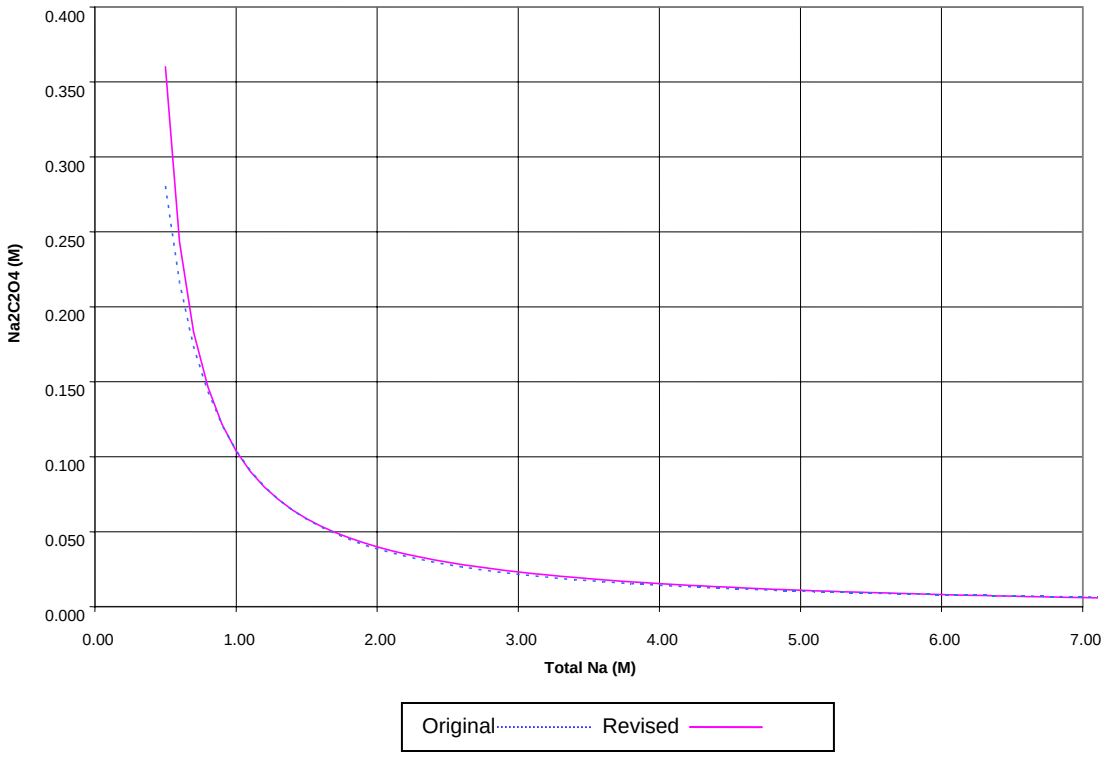

Figure 2 Oxalate Solubility as a Function of Sodium Concentration

As shown in Figure 2, as the sodium concentration increases past about 1.5 M, the solubility of sodium oxalate quickly decreases (Ref. 9). Except for flushing and washing activities, the routine sodium concentration in the HLW system is normally in excess of 6 molar (Ref. 5). Almost all of the soluble oxalate entering the *D-Evaporator Drop Tank* would precipitate, as the evaporator attainment proportionately increases the sodium concentration.

Table 3 shows the developed oxalate balance. The *#1 Sludge Heel-Solid* and the *#5 Feed Slurry-Solid* are included only for comparative purposes.

Table 3 Oxalate Balance

Stream	*# 1 Sludge Heel*	*#5 Feed Slurry*	*#6 Remaining Solution*	*#7 Spent Wash Water*	*#8 Combined Evaporator Solution*
Phase	*Solid*	*Solid*	*Solid*	*Solid*	*Solid*
Weight					
Total kg	9.4E+3	3.2E+4	NA	NA	NA
NaC2O4 kg	0	2.2E+4	2.7E+3	3.0E+3	5.7E+3

By comparing the *#1 Sludge Heel-Solid* (total kg), to the *#5 Feed Slurry-Solid* (total kg) and the *#8 Combined Evaporator Solution-Solid* (sodium oxalate kg), for every 1 kg of sludge solid dissolved, 3.4 kg of resultant solids would be required to be sent to DWPF, and about 0.6 kg of oxalate solids (or based on a ratio to the pH Restoration tank, about 0.9 total kg solids) would form in the *Evaporator Drop Tank*.

Potential Impacts

Based on above material balance, a list of potential process impacts was developed, and screened, and then evaluated for acceptability. For the screening, any impact which could not be discounted with an available reference was considered to screen as "*Yes,*" thereby indicating a need for further evaluation. The screening results are summarized in Table 4, below.

Table 4 Impact Screening For Oxalic Acid Cleaning

A- Treatment Tank	Potential Impact	*B- pH Restoration Tank*	Potential Impact	*C- DWPF Feed Tank*	Potential Impact	*D- Evaporator Drop Tank*	Potential Impact
significant CO2 release	yes	significant CO2 release	no	additional blending required	yes	large oxalate heel forms	Yes
flammability from H2 from corrosion & radiolysis	yes	flammability from h2 from corrosion & radiolysis	no	additional rinsing required	yes	decrease in evaporator attainment	Yes
overheating from heat of reaction	yes	overheating from heat of dilution	yes	more glass canisters required	yes		
floating layer	no (Ref.4)	floating layer	yes	more oxalate feed qualification required	no		
Rheology change	no (Ref. 4)	rheology change	no (Ref. 4)				
energetic compounds	yes	energetic compounds	yes				

The impacts which screened “yes” were further evaluated, as summarized in Table 5.

Table 5 Impact Evaluation For Oxalic Acid Cleaning

Location	Impact	Evaluation	Acceptable?
A. Treatment Tank	Flammability from H2 from Corrosion	Ventilation system upgrades may be required, and will require further evaluation; however, compared to nitric acid or peroxide, oxalic acid is considered to have the lowest hydrogen generation rate from corrosion.	Yes Not an Issue
	Significant CO2 Release	Ventilation system required for hydrogen would be designed for CO2.	Yes Not an Issue
	Overheating from heat of reaction	This has been determined to be insignificant based on testing. In addition, the oxalic acid addition rate would be slowed, and increased cooling capacity could be provided if temperature begins to significantly increase.	Yes Not an Issue (Ref. 9)
B. pH Restoration Tank	Overheating from heat of dilution	This has been determined to be insignificant based on testing. The dissolved heel transfer rate would be slowed, and increased cooling capacity would be provided if temperature begins to significantly increase.	Yes Not an Issue (Ref. 9)
C. DWPF Feed Tank	Additional Blending of sludge required	If blending is required causing the waste to remain in a non-agitated tank for more than 5 years, there is a reasonable chance that the sodium oxalates would form an insoluble salt heel that could not be easily removed. Increased uncertainty to feed to DWPF. The batch quantification process normally takes 1 year. Some additional batch qualification time required. Based on clever batching strategies up to 3 cans of oxalate can be added to s sludge batch without producing additional canisters.	Yes But must be managed. (Ref. 6)
	Additional Washing Required	Additional washing to the 1 molar sodium, the historic sodium level for feed to DWPF, would cause a large fraction of the oxalates to solubilize. Ultimately, the oxalates would form additional insoluble salt heels. Based on clever batching strategies up to 3 cans of oxalate can be added to sludge batch without producing additional canisters.	Yes But must be managed (Ref. 6)
	Addition cans produced	Based on clever batching strategies up to 3 cans of oxalate can be added to sludge batch without producing additional canisters.	Yes But must be managed (Ref. 6)
D. Evaporator Drop Tank	Large Oxalate Heel Forms	The formation of a small heel within the evaporator drop tank may be acceptable; however, if the heel increases by more than a few inches, the increase could noticeably effect the capacity of the tank, and therefore also effect the operation of the evaporator. Overall, there are no current technologies that have been evaluated or deemed acceptable for salt heel removal.	Yes But must be managed (Ref. 6)
	Evap Operation	Evaporator operation will be impacted only if the *#6 Remaining Solution* of the *#7 Spent Wash Water* is sent to the Evaporator Feed Tank. This can be managed by procedurally requiring that both streams are sent to the evaporator drop tank.	Yes But must be managed (Ref.6)

From Table 5, we can see that for the *A-Treatment Tank* and *B-pH Restoration Tank*, the impact can be considered acceptable with some upgrades or additional studies required. For the *#9 Oxalate DWPF Feed* and for the *C-Evaporator Drop Tank*, the impacts are acceptable but will need to be managed. Specifically, only a few tanks should be cleaned during any sludge batch, transfers should be well controlled (i.e., potentially significant impact from an inadvertent transfer), and oxalate solids produced in *B-pH Restoration Tank* should not be stored for long periods of time, but transferred quickly to a pre-washed, pre-qualified sludge batch.

CONCLUSIONS

Overall, assuming no process upsets, for every 1kg of sludge solid dissolved from the *Treatment Tank* using oxalic acid, about 3.4 kg of solids will precipitate and need to be processed through DWPF, while about 0.6 kg of sodium oxalate will precipitate out in the evaporator system.

The impacts associated with the *Treatment Tank* and *ph Restoration Tank*, can be considered acceptable pending ventilation upgrades or additional studies. Assuming a maximum of 3 tanks heels are cleaned per sludge batch, the impacts on *DWPF feed* and the *D-Evaporator Drop* tank can also be deemed acceptable. However, associated with the *DWPF feed* and the *D-Evaporator Drop Tank*, oxalic acid cleaning with subsequent pH restoration will result in long term impacts that will need to be managed.

RECOMMENDATIONS

The impacts from oxalic acid cleaning that require long term management are largely associated with the pH restoration and not the actual cleaning. Knowing that oxalate destruction methods are employed in various other industries (Ref. 10), the use of oxalate destruction technologies may be beneficial and should also be further considered.

REFERENCES

1. Legler, B.M., and Bray, G.RE.: Chemical Engineering Progress 72: 52, Mar. 1976

2. Adu-Wusu, K., Barnes, M., Bibler. N., Cantrell, J., Fondeur, F., Hamm, B., Herman, C., Hobbs, D., Ketusky, E, Singleton, M., Stallings, M., Stevens, W., and Wiersma, B.; "Waste Tank Heel Chemical Cleaning Summary," WSRC-TR-2003-00401, Rev.0, Washington Savannah River Site, South Carolina, Sept. 2003.

3. Hobbs, D.T., Stallings, M.E., and Wiersma, B.J.; "Dissolution of Simulated and Radioactive Savannah River Site High Level Waste Sludge with Oxalic Acid and Citric Acid Solutions," WSRC-TR-2004-00043, Rev. 1, Washington Savannah River Site, South Carolina, July 2004.

4. West, W.I.; "Tank 16 Demonstration Water Wash and Chemical Cleaning Results," DPSP: 80-17-23, Rev. 0, Washington Savannah River Site, South Carolina, December 16, 1980.

5. Hester, R.; "High Level Waste Characterization System (WCS)", WSRC-TR-96-0264, Rev. 0, Washington Savannah River Site, South Carolina, December 1996.

6. Ketusky, E.T.; "Engineering Study, System and Process Impact Study for Using Oxalic acid for the Tank 8 Sludge Heel Removal," X-ESR-F-00049, Rev. 0, Washington Savannah River Site, South Carolina, Nov. 2004.

7. Pike, J.A., Badheka, N.P., and Ketusky, E.T.; "Flowsheet for SRS Waste Tank Heel Removal Using Oxalic Acid," WSRC-TR-2004-00317, Washington Savannah River Site, South Carolina, Nov. 2004.

8. Herman, D.T.; "Investigating Hydrogen Generation and Corrosion in the Treatment Tank and the Potential Formation Of A Floating Layer in Neutralization Tank During Waste

Tank Heel Chemical Cleaning," WSRC-STI-2007-00209, Rev. 0, Washington Savannah River Site, South Carolina, April, 2007.

9. Kilpatrick, L.L. "Solubility of Sodium Oxalate and Sodium Tetraphenylborate in DWPF Supernate," DPST-84-341, Washington Savannah River Site, South Carolina, February 28, 1984.

10. Quici, N.; Morgada, M.E.; Piperata, G.; Babay,P.; Gettar, R,: and Litter, M.I.,; "Oxalic acid Destruction At High Concentrations by Combined Heterogeneous Photocatalysis And Photo-Fenton Processes ,"Unidad de Actividad Química, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, 1650 San Martín, Prov. de Buenos Aires, Argentina, April 1, 2005.